

# Nonequilibrium density matrix in quantum open systems: generalisation for simultaneous heat and charge steady-state transport

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We suggest a generalisation of the expression of the nonequilibrium density matrix obtained by Hershfield's method for the cases where both heat and charge steady state currents are present in a quantum open system. The finite-size quantum system, connected to two temperature and particle reservoirs, is driven out of equilibrium by the presence of both a temperature gradient and a chemical potential gradient between the two reservoirs. We show that the NE density matrix is given by a generalised Gibbs-like ensemble, and is in full agreement with the general results of the McLennan-Zubarev nonequilibrium ensembles. The extra non-equilibrium terms are related to the entropy production in the system and characterise the fluxes of heat and particle. An explicit example, for the lowest order expansion, is provided for a model system of non-interacting fermions.

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## I. INTRODUCTION

When a finite-size quantum system is put into contact with different macroscopic temperature and/or particle reservoirs (each at their own equilibrium), the system will reach a non-equilibrium (NE) time-independent steady state after some time (which is much longer than some typical relaxation times of the finite system). The steady state is obtained from the balance between irreversible processes and the driving forces induced by the macroscopic reservoirs.

The understanding of such irreversible phenomena and of the corresponding NE steady state is a long-standing problem in statistical mechanics. The NE steady state can be seen as its equilibrium counterpart for different external constraints, in the sense that an equilibrium state represents a stationary state of a closed system, while the NE steady state is the time-invariant state of an open system. This is why the construction of Gibbs-like ensembles for the NE steady state has been explored by many authors. Early attempts, going beyond linear response<sup>1</sup>, have been performed by McLennan<sup>2</sup> for classical systems and by Zubarev<sup>3-7</sup> for both classic and quantum systems. In such approaches, the Gibbsian statistical mechanics method is extended to include steady-state NE conditions in the density matrix leading to the so-called NE statistical operator method (NESOM). More rigorous analysis of the existence and stability of the NE steady state have been performed using  $C^*$  algebraic methods<sup>8-16</sup>. The existence of conducting steady states has also been critically discussed in Refs. [17,18] by using different levels of approximation for the many-body effects in NE Green's functions approaches and time-dependent density functional theory.

A reformulation of NE steady state quantum statistical mechanics has been proposed by Hershfield in Ref. [19]. An explicit expression for the NE density matrix was derived for a system at a unique temperature in the presence of an applied bias between two electrodes. A

scheme upon which one can build non-perturbative calculations was also provided. Such an approach has been successfully applied in numerical calculations of quantum electron transport<sup>20-28</sup>. The universal aspects of NE currents in a quantum dot has also been explored by Doyon et al. in a somewhat different, but related, approach<sup>29</sup>. Another approach to calculate the asymptotic form of operators in NE quantum systems is given in Ref. [30]. However, in these approaches, only charge current was considered. The whole system is at a unique temperature and cannot support any other energy/heat transport processes, happening in parallel with quantum charge transport.

Furthermore, a generalisation of Hershfield scheme to the full time dependent problem with arbitrary initial conditions is provided in Ref. [31]. In this work, the author uses the formal scattering approach of Lippmann and Schwinger<sup>32</sup> to construct the time-dependent NE density matrix. The construction of such a NE density matrix should also be valid for leads at different temperatures, although this point was not explicitly addressed in Ref.[31]. One of the important outputs of this work is that the time-dependent NE density matrix is variational and therefore one can set up an efficient single-particle evaluation scheme for the steady-state Hershfield form<sup>33,34</sup>.

However, the connection between the NESOM and the previous NE density matrix scheme was overlooked by the author of Refs.[19,31]. We address such a connection (for the steady state) in an explicitly and rigorous manner in the present paper.

We suggest an extension of the approach originally developed by Hershfield, to more general NE conditions: the presence of both a temperature and chemical potential gradients between two electrodes connected to the quantum open system. We show how to construct a NE density matrix when the two reservoirs are at two different temperatures and at two different chemical potentials. For that, we use some concepts developed for

asymptotic steady-state operators in Ref. [29,30,35,36], along the lines of the original work of Hershfield<sup>19</sup>. We obtain the generalised Gibbs-like expression for the corresponding NE density matrix. The extra NE terms (extra from an equilibrium grand-canonical density matrix) characterise the entropy production in the open system and are related to the fluxes of particle and heat. We also show that the generalised NE density matrix for the steady-state is fully compatible with the NESOM of Zubarev<sup>36</sup>.

The paper is organised as follows. In Sec. II, we show how the NE density matrix can be expressed in terms of asymptotic scattering operators. We discuss in details the choice of the initial conditions and partition of the system. We also provide a central result for an iterative expansion of asymptotic steady-state operators. In Sec. III, we use this result to rederive the original expression of NE density matrix for a system at a unique temperature. We postulate a generalisation of the NE density matrix for conditions including both heat and charge currents in Sec. IV. A rigorous proof of the equivalent between our generalised NE density matrix and the more general McLennan-Zubarev NE statistical operator is given in Sec. V. An explicitly example of the calculation of the NE density matrix for a model system is given in Sec. VI. Conclusion are presented in Sec. VII. Some central mathematical expressions used to derive our results are provided in the Appendices.

## II. NON-EQUILIBRIUM DENSITY MATRIX FROM ASYMPTOTIC SCATTERING TECHNIQUES

### A. Generalities

The average of an arbitrary operator  $X$  is given by

$$\langle X(t) \rangle = \text{Tr}[\rho_0 X(t)] = \text{Tr}[\rho(t) X], \quad (1)$$

where the density matrix  $\rho$ , solution of the Liouville equation, is given by

$$\rho(t) = e^{-iH(t-t_0)} \rho_0 e^{iH(t-t_0)}. \quad (2)$$

Here  $H$  is the total Hamiltonian of the system and  $\rho_0$  is the initial density matrix at time  $t_0$ . The trace in Eq. (1) is taken over the appropriate degree of freedom characterising the entire system.

Eq. (1) can be re-arrange by using the property of cyclic permutation of the trace and the fact that the total Hamiltonian can be split into two parts:  $H = H_0 + W$ , with a reference Hamiltonian  $H_0$  (for example an unperturbed Hamiltonian), and a perturbation  $W$ . We have,

using  $u = t - t_0$ , the following expression:

$$\begin{aligned} \langle X(t) \rangle &= \text{Tr}[\rho_0 e^{iH_0 u} X e^{-iH_0 u}] \\ &= \text{Tr}[e^{-iH_0 u} \rho_0 e^{iH_0 u} X] \\ &= \text{Tr}[\rho_0 e^{iH_0 u} e^{-iH_0 u} e^{iH_0 u} X e^{-iH_0 u}] \\ &= \text{Tr}[\tilde{S}(\tau) \rho_0 \tilde{S}^{-1}(\tau) X], \end{aligned} \quad (3)$$

where we use the fact that  $\rho_0$  commutes with  $H_0$  and introduce the notation  $\tau = -u$  and  $\tilde{S}(\tau) = e^{iH\tau} e^{-iH_0\tau}$  [37].

### B. Set-up and initial conditions

We consider a (finite size) central region  $C$ , connected two electrodes (left  $L$  and right  $R$ ) acting as thermal and particle reservoirs. These electrodes are described within the thermodynamics limits, i.e. they are macroscopic (semi infinite). Initially they are at their own equilibrium, characterized by two temperatures  $T_L$  and  $T_R$ , and by two chemical potentials  $\mu_L$  and  $\mu_R$ . Furthermore, we ignore the interaction between particles in the electrodes, although the central region  $C$  may contain such kind of interaction.

We are interested in steady state regime, and therefore we take the initial state of the system to be in the far remote past  $t_0 \rightarrow -\infty$ . The system is then characterised by an Hamiltonian  $H_0$ . After all parts of the system are “connected” and after some time elapses, the full system is considered to reach a NE steady state. The system is then characterised (at time  $t$ ) by an total Hamiltonian  $H = H_0 + W$ . This time  $t$  is considered to be the “now” time (we might take it to be  $t = 0$  in the following, but only for convenience) and  $t$  is far enough from  $t_0$  so that all the interactions act fully on the system.

The questions related to the possibility of reaching a NE steady-state have been addressed in Refs. [8–15]. It is also been argued that a system will always reach a steady-state if it is a (or if it is connected to another) system in the thermodynamic limit regardless the presence (or absence) of adiabatic switching of the interactions<sup>15,38,39</sup>.

We are now facing different possible choices to perform the separation of the full Hamiltonian into  $H_0$  and  $W$ . We know that the full system is described by

$$H = \sum_{\alpha=L,R} (H_\alpha + V_{\alpha C} + V_{C\alpha}) + H_C^0 + V_C^{\text{int}}, \quad (4)$$

where  $H_\alpha, H_C^0$  are the non-interacting Hamiltonians of the  $\alpha = L, R$  electrodes and of the central region  $C$  respectively. The interaction between particles in region  $C$  is given by  $V_C^{\text{int}}$  and the coupling between region  $C$  and the  $\alpha$  electrode is given by  $V_{\alpha C}$ . We also consider that all the non-interacting Hamiltonians,  $H_L, H_C^0, H_R$ , commute with each other and with the occupation numbers  $N_\beta$  ( $\beta = L, C, R$ ). The commutators between the interaction part  $V = V_C^{\text{int}} + \sum_\alpha (V_{\alpha C} + V_{C\alpha})$  and  $N_\beta$  does not vanish, i.e.  $[V, N_\beta] \neq 0$ .

There are basically two families of approaches: the partitioning and the partition-free schemes. In the latter<sup>40,41</sup>, the three  $L, C, R$  regions are initially connected and all at equilibrium, i.e. initially, there is one single  $T$  and one single  $\mu^{\text{eq}}$ . The applied bias between the electrodes is then introduced under the form of an external potential. The interaction between particles in the central region  $C$  could be introduced in either the initial Hamiltonian  $H_0$  or in the “coupling” term  $W$ . Such an approach has been successfully applied for studying quantum electron transport in systems at a single temperature<sup>41,42</sup>. However, it does not seem particularly well adapted for the study of both energy/heat and charge transport. The introduction of a temperature gradient between the electrodes in the partition-free method appears difficult to perform, especially in the form of an external perturbation on the electron system.

Therefore, we focus here on the second kind of approaches based on partitioning the system. Initially, all regions  $L, C, R$  are separated and are at their own equilibrium. The macroscopic  $L$  and  $R$  regions are represented by a density matrix  $\rho_{L,R}$  expressed in the grand canonical ensemble, with temperature  $T_\alpha = 1/k\beta_\alpha$  and chemical potential  $\mu_\alpha$ . The initial density matrix of the central region is assumed to take any arbitrary form  $\rho_C$  as this region is not in the thermodynamic limit.

There are still two ways to partition the system: Case (a) we take the non-interacting Hamiltonian  $H_0$  to be defined by  $H_0 = H_L + H_R$  and for the perturbation  $W = H_C^0 + V_C^{\text{int}} + \sum_\alpha (V_{\alpha C} + V_{C\alpha})$ . Therefore, we have for the initial density matrix  $\rho_0 = \rho_L \otimes \rho_R$ . Case (b) we take for  $H_0$  all the non-interacting Hamiltonians of the three regions  $H_0 = H_L + H_C^0 + H_R$  and  $W = V_C^{\text{int}} + \sum_\alpha (V_{\alpha C} + V_{C\alpha})$  contains only the coupling/interaction terms. In this case, we have for the initial density matrix  $\rho_0 = \rho_L \otimes \rho_C \otimes \rho_R$ . The question that arises now is the following: how should be defined the density matrix  $\rho_C$  for the central region?

In the set-up we want to study,  $\rho_C$  cannot be given by a canonical or a grand canonical ensemble. Otherwise it would imply the presence of the third reservoir characterised by its own temperature (and chemical potential). Therefore, we need to define  $\rho_C$  from a microcanonical ensemble. The density matrix  $\rho_C$  can be given either in a pure state representation  $\rho_C = |\Psi_C\rangle\langle\Psi_C|$ , where the ket  $|\Psi_C\rangle$  represents any linear combination of the states  $|n\rangle$  of the central region  $C$ , or in a mixed state representation  $\rho_C = \sum_n w_n |n\rangle\langle n|$ , with probabilities  $w_n$  such as  $\sum_n w_n = 1$ . The probabilities  $w_n$  are not given by a Boltzmann or Gibbs factor since they are not obtained from a canonical or grand canonical ensemble.

The choice of the initial preparation ( $\{w_n\}$ ) of the central region seems quite arbitrary. However, we know that for the long time limit, when a system has reached a steady-state after an applied perturbation, the initial correlations vanishes and a single steady-state is reached regardless to the choice of initial conditions<sup>8–15</sup>. Therefore any particular choice of the initial density matrix

$\rho_C$  is not relevant. This is however not the case for the transient regime<sup>43,44</sup>.

Since we want to expand the results of Hershfield to heat and charge transport, as well as the results of Ref. [35] to the presence of a central region between the two electrodes, we are choosing similar initial conditions as in Ref. [35]. Hence we take the option (a) for the partitioning of the system, i.e.  $H_0 = H_L + H_R$  and  $W = H_C^0 + V_C^{\text{int}} + \sum_\alpha (V_{\alpha C} + V_{C\alpha})$ .

One should note that case (a) is related to case (b) when one takes, for initial condition for the central region, a density matrix  $\rho_C$  with zero matrix elements (diagonal matrix for a mixed state representation). In other words, we consider that initially the central region is empty of electrons. The initial matrix density  $\rho_0$  has then a block of zeros in the subspace of the central region  $C$  and the matrix elements of  $\rho_\alpha$  in the subspaces of the  $\alpha = L, R$  electrodes. In the asymptotic limit, the NE density matrix will have matrix elements spreading over all the three different subspaces. Since the NE density matrix is independent of the initial conditions in the steady state<sup>8–15</sup>, one can take a convenient choice for the initial conditions that makes the derivations more easily tractable<sup>45</sup>.

Finally, the left and right electrodes are prepared in a Gibbs grand-canonical ensemble with density matrices  $\rho_\alpha$  ( $\alpha = L, R$ )

$$\rho_\alpha = \frac{1}{Z_\alpha} e^{-\beta_\alpha (H_\alpha - \mu_\alpha N_\alpha)}, \quad (5)$$

with  $Z_\alpha = \text{Tr}[e^{-\beta_\alpha (H_\alpha - \mu_\alpha N_\alpha)}]$ . By definition, we have  $[H_\alpha, H_\beta] = 0$  and  $[H_\alpha, N_\beta] = 0$ , hence

$$\rho_0 = \rho_L \otimes \rho_R = \frac{1}{Z} e^{-\sum_\alpha \beta_\alpha (H_\alpha - \mu_\alpha N_\alpha)}, \quad (6)$$

where  $Z = \text{Tr}[e^{-\sum_\alpha \beta_\alpha (H_\alpha - \mu_\alpha N_\alpha)}]$ .

### C. Asymptotic steady-state NE density matrix

For the asymptotic steady state regime, we consider that the time different  $u = t - t_0$  goes to  $\infty$  in Eq. (3), hence  $\tau \rightarrow -\infty$ . This means that either the time  $t$  is fixed and the initial time  $t_0$  is the far remote past  $t_0 \rightarrow -\infty$ , or  $t_0$  is fixed and  $t$  is the far remote future. In this case, the average for the NE asymptotic steady state is obtained from

$$\begin{aligned} \langle X \rangle^{\text{NE}} &= \lim_{u \rightarrow +\infty} \text{Tr}[e^{-iH_u} \rho_0 e^{iH_u} X] \\ &= \lim_{\tau \rightarrow -\infty} \text{Tr}[\bar{S}(\tau) \rho_0 \bar{S}^{-1}(\tau) X] \\ &= \text{Tr}[\Omega^{(+)} \rho_0 \Omega^{(+)-1} X] \\ &= \text{Tr}[\rho^{\text{NE}} X], \end{aligned} \quad (7)$$

where we use the definition of the Møller operator<sup>46–49</sup>

$$\Omega^{(+)} = \lim_{\tau \rightarrow -\infty} e^{iH\tau} e^{-iH_0\tau}. \quad (8)$$

In Appendix A, we recall some definitions of the Møller operators and prove one of their important properties: the intertwining relations. Such a relation connects the non-interacting Hamiltonian  $H_0$  to the full Hamiltonian:  $\Omega^{(+)}H_0 = H\Omega^{(+)}$ .

The NE density matrix  $\rho^{\text{NE}}$  in the steady state is obtained as<sup>35,36</sup>:

$$\begin{aligned}\rho^{\text{NE}} &= \Omega^{(+)}\rho_0\Omega^{(+)-1} \\ &= \frac{1}{Z}e^{-\beta_L(H_L^+ - \mu_L N_L^+) - \beta_R(H_R^+ - \mu_R N_R^+)},\end{aligned}\quad (9)$$

where the asymptotic operator  $X^+$  is defined as  $X^+ = \Omega^{(+)}X\Omega^{(+)-1}$  for any operator  $X$ .

Eq. (9) is the starting point for deriving the NE density matrix in the form given by Hershfield and for providing a generalisation to the cases including temperature gradients ( $\beta_L \neq \beta_R$ ) and applied biases ( $\mu_L \neq \mu_R$ ). For completing our derivations, we use an important identity:

$$\begin{aligned}H_L^+ + H_R^+ &= \Omega^{(+)}(H_L + H_R)\Omega^{(+)-1} = \Omega^{(+)}H_0\Omega^{(+)-1} \\ &= H\Omega^{(+)}\Omega^{(+)-1} = H.\end{aligned}\quad (10)$$

### III. CHARGE CURRENT AT A UNIQUE TEMPERATURE

For a system at a unique temperature ( $\beta_L = \beta_R$ ) and with an applied bias ( $\mu_L \neq \mu_R$ ), the NE density matrix, given in Eq. (9), is rewritten as:

$$\begin{aligned}\rho^{\text{NE}} &= e^{-\beta(H_L^+ + H_R^+ - \mu_L N_L^+ - \mu_R N_R^+)}/Z \\ &= \frac{1}{Z}e^{-\beta(H - \Upsilon)},\end{aligned}\quad (11)$$

where

$$\begin{aligned}\Upsilon &= \mu_L N_L^+ + \mu_R N_R^+ = \Omega^{(+)}Y_0\Omega^{(+)-1}, \\ Y_0 &= \mu_L N_L + \mu_R N_R.\end{aligned}\quad (12)$$

Eq. (11) has just the same form as the NE density matrix developed by Hershfield in [19]. This result suggests that a series expansion of the asymptotic operator  $\Upsilon = \Omega^{(+)}Y_0\Omega^{(+)-1}$  can be obtained following the prescriptions given in the original paper of Hershfield [19]. Hence the  $\Upsilon$  operator in Eq. (11) and Hershfield  $Y$  operator can be determined from the same iterative scheme. Therefore we have  $\Upsilon = \sum_n \Upsilon_{n,I}$  with  $\Upsilon_{n,I}(t)$  following the iterative relation

$$\partial_t \Upsilon_{n+1,I}(t) = -i[\tilde{W}_I(t), \Upsilon_{n,I}(t)], \quad (13)$$

where the operators are given in the interaction representation,  $X_I(t) = e^{iH_0 t} X e^{-iH_0 t}$  ( $\tilde{W}_I$  includes the adiabatic factor  $\tilde{W}_I(t) = e^{-\eta|t|} e^{iH_0 t} W e^{-iH_0 t}$ ) and with the initial value  $\Upsilon_{0,I} = Y_0$  since  $Y_0$  commutes with  $H_0$ <sup>50</sup>.

It should be noted that the construction of the NE density matrix for a system at unique temperature can also be found in Ref. [31]. This paper provides a simpler explicit, but more formal, construction of the general time-dependent NE density matrix by using scattering theory and the full time evolution operator. The steady-state properties are recovered as an asymptotic limit.

Finally, we can check an important property of the  $\Upsilon$  operator. Since  $\Upsilon$  is a linear superposition of the operators  $N_\alpha^+$  ( $\alpha = L, R$ ), we have

$$\begin{aligned}[N_\alpha^+, H] &= \Omega^{(+)}N_\alpha\Omega^{(+)-1}H - H\Omega^{(+)}N_\alpha\Omega^{(+)-1} \\ &= \Omega^{(+)}N_\alpha H_0\Omega^{(+)-1} - \Omega^{(+)}H_0 N_\alpha\Omega^{(+)-1} \\ &= \Omega^{(+)}[N_\alpha, H_0]\Omega^{(+)-1} = 0,\end{aligned}\quad (14)$$

as by definition  $N_\alpha$  commutes with the non-interacting Hamiltonian  $H_0$ . Therefore the operator  $\Upsilon(t) = \Upsilon$  is a constant of motion (a conserved quantity), with respect to the total Hamiltonian  $H$ . And the NE density matrix  $\rho^{\text{NE}}$ , given by Eq. (11), is indeed a time-independent density matrix, as expected for the steady state<sup>51</sup>.

### IV. SIMULTANEOUS HEAT AND CHARGE CURRENTS

In the presence of both a temperature gradient and a chemical potential gradient ( $\beta_L \neq \beta_R$ ,  $\mu_L \neq \mu_R$ ), there is a simultaneous flow of energy/heat and charge between the two electrodes, through the central region  $C$ .

We reformulate the general expression of the NE density matrix Eq. (9) by introducing first an average temperature<sup>35</sup>, via an average  $\bar{\beta}$  defined by  $\bar{\beta} = (\beta_L + \beta_R)/2$ . Hence, the exponent in Eq. (9) becomes:

$$\begin{aligned}&-\beta_L(H_L^+ - \mu_L N_L^+) - \beta_R(H_R^+ - \mu_R N_R^+) \\ &= -\bar{\beta}(H_L^+ + H_R^+) + (\bar{\beta} - \beta_L)H_L^+ + (\bar{\beta} - \beta_R)H_R^+ + \bar{\beta}Y^Q \\ &= -\bar{\beta}(H_L^+ + H_R^+) - \bar{\beta}Y^E + \bar{\beta}Y^Q,\end{aligned}\quad (15)$$

where

$$\begin{aligned}\bar{\beta}Y^Q &= (\beta_L \mu_L N_L^+ + \beta_R \mu_R N_R^+), \\ \bar{\beta}Y^E &= (\beta_L - \beta_R)\frac{1}{2}(H_L^+ - H_R^+).\end{aligned}\quad (16)$$

The NE density matrix can be rewritten as follows

$$\rho^{\text{NE}} = \frac{1}{Z}e^{-\bar{\beta}(H - Y^Q + Y^E)}. \quad (17)$$

Note that in Eq. (17), the generalised Gibbs-like form of the NE density matrix is given with an effective temperature  $\bar{T}$  defined from  $\bar{\beta}$ . This temperature is different from the temperature of the left or right electrodes  $T_{L,R}$  since  $\bar{T} = 1/k_B\bar{\beta} = 2T_L T_R / (T_L + T_R)$ .

The two quantities  $Y^Q$  and  $Y^E$  follow the same formal expression, i.e.  $Y^x = c_L X_L^+ + c_R X_R^+ = \Omega^{(+)}(c_L X_L +$



$c_R X_R) \Omega^{(+)-1}$ , with  $X_\alpha = N_\alpha (H_\alpha)$  for  $Y^Q$  ( $Y^E$  respectively). Furthermore, Eq. (17) has also the same formal structure of a generalised Gibbs ensemble as originally obtained by Hershfield.

We then suggest that the two quantities  $Y^{Q,E}$  can be obtained from the same formal iterative scheme:

$$\begin{aligned} Y^{Q,E} &= \sum_n Y_{n,I}^{Q,E}, \\ \partial_t Y_{n+1,I}^{Q,E}(t) &= -i[\tilde{W}_I(t), Y_{n,I}^{Q,E}(t)] \end{aligned} \quad (18)$$

with the initial values<sup>55</sup>

$$\begin{aligned} Y_{0,I}^Q &= Y_0^Q = a_L^Q N_L + a_R^Q N_R, \\ Y_{0,I}^E &= Y_0^E = a^E (H_L - H_R), \end{aligned} \quad (19)$$

and

$$\begin{aligned} a_\alpha^Q &= \frac{2\beta_\alpha \mu_\alpha}{\beta_L + \beta_R} \\ a^E &= \frac{\beta_L - \beta_R}{\beta_L + \beta_R}. \end{aligned} \quad (20)$$

Eq. (17) and the iterative scheme, Eqs. (18,19) for  $Y^{Q,E}$ , are the main results of the paper. We prove exact their formal equivalence with the McLennan-Zubarev form of the NE density in the following section. We also provide a concrete example for deriving the expression of the NE density matrix for a model system in Sec. VI.

The equations Eqs. (17,18,19) correspond to the most general expression of the steady-state NE density matrix in the presence of both heat and charge currents for a two-reservoir device.

As shown in the previous section,  $Y^Q$  is a constant of motion since it commutes with the total Hamiltonian  $H$ . It is easy to show that  $Y^E$  is also a constant of motion (a conserved quantity), since  $[H_\alpha^+, H] = \Omega^{(+)}[H_\alpha, H_0]\Omega^{(+)-1} = 0$ .

At equilibrium,  $\beta_L = \beta_R$  hence  $Y^E$  vanishes because  $a^E = 0$ . There is a single chemical potential  $\mu_L = \mu_R = \mu^{\text{eq}}$  and  $Y^Q = \mu^{\text{eq}}(N_L^+ + N_R^+)$  [56]. Hence one recovers the usual Gibbs form for the equilibrium density matrix in a grand-canonical ensemble  $\rho^{\text{eq}} = e^{-\beta(H - \mu^{\text{eq}}N)}/Z$ , as expected.

It is important to note that  $Y^Q$  exists because of the presence of the two different chemical potentials  $\mu_{L,R}$  and hence it is related to the charge current. The quantity  $Y^E$  exists because of the presence of the temperature gradient  $(\beta_L - \beta_R)$  and hence is related to the energy/heat flow between the electrodes. Indeed, following Ref. [35], we have

$$\begin{aligned} Y^E &= \frac{\beta_L - \beta_R}{\beta} E^+, \\ E^+ &= \Omega^{(+)} E \Omega^{(+)-1}, \\ E &= \frac{1}{2}(H_L - H_R). \end{aligned} \quad (21)$$

In the Heisenberg representation, the energy current operator is given by  $j_E(t) = \partial_t E(t) = i[H, E(t)]$  and

$E(t) = \int_{-\infty}^t j_E(u) du$ . We assume that there is not current at  $t_0 = -\infty$  since the system is decoupled, and the interaction Hamiltonian  $W$  vanishes. Furthermore, the operator  $Y^Q$  can be rewritten as

$$\begin{aligned} Y^Q &= \bar{\mu} N + \frac{\Delta_\mu}{\beta} Q^+, \\ \bar{\mu} &= (\beta_L \mu_L + \beta_R \mu_R) / (\beta_L + \beta_R), \\ \Delta_\mu &= \beta_L \mu_L - \beta_R \mu_R, \end{aligned} \quad (22)$$

and

$$\begin{aligned} Q^+ &= \Omega^{(+)} Q \Omega^{(+)-1}, \\ Q &= \frac{1}{2}(N_L - N_R). \end{aligned} \quad (23)$$

The charge current operator  $j_Q(t)$  is related to the quantity  $Q$  as  $j_Q(t) = \partial_t Q(t) = i[H, Q(t)]$  and  $Q(t) = \int_{-\infty}^t j_Q(u) du$  (no current at  $t_0 = -\infty$  since the system is decoupled). The two quantities  $Y^{Q,E}$  are now clearly related to the charge and heat flows induced by the NE conditions. They are also associated with the entropy production in the system<sup>52,53</sup>. For the time dependent problem considered in Ref. [31] for a system at a unique temperature, it was shown that the operator  $Y$  describes how the Gibbs free energy evolves as the interaction  $W$  is adiabatically turned on.

## V. CONNECTION WITH THE MCLENNAN-ZUBAREV NE STATISTICAL OPERATOR

In this section, we show the formal connection between of suggested generalisation of the NE density matrix Eq. (17) and the McLennan-Zubarev NE statistical operator.

In Ref. [52], we have shown that the original approach of Hershfield provides a NE density matrix, see Eq. (11), which is a subset of the more general NE density matrix given by the McLennan-Zubarev method.

The generalised NE density matrix Eq. (17) is fully compatible with the McLennan-Zubarev NE statistical operator method (NESOM). Indeed, the quantities  $E(t)$  and  $Q(t)$ , related to the operators  $Y^{E,Q}$  respectively, are expressed in terms of the time integral  $\int_{-\infty}^0 J_S(u) du$  entering the definition of the the McLennan-Zubarev NE statistical operator<sup>4,11,52</sup>. The latter is given by<sup>54</sup>

$$\begin{aligned} \rho^{\text{NESO}} &= \frac{1}{Z} \exp \left\{ - \sum_\alpha \beta_\alpha (H_\alpha - \mu_\alpha N_\alpha) \right. \\ &\quad \left. + \int_{-\infty}^0 ds e^{\eta s} J_S(s) \right\}. \end{aligned} \quad (24)$$

The quantity  $J_S(u)$  is called the non-systematic energy flows<sup>11</sup> and is related to the entropy production rate of

the system<sup>52</sup>. It is given by

$$\begin{aligned} J_S(s) &= \sum_{\alpha} \beta_{\alpha} J_{\alpha}^q(s), \\ J_{\alpha}^q(s) &= \frac{d}{du} (H_{\alpha}(s) - \mu_{\alpha} N_{\alpha}(s)) \end{aligned} \quad (25)$$

where all operators are given in the Heisenberg representation.

The concept of the non-systematic energy flows in the NESOM is also consistent with the Gibbs free energy description given in Ref. [31] (in this work, the variational for the NE density matrix and the corresponding thermodynamic grand potential corresponds to an entropy maximization principle, constrained by both the particle flow effects and the internal energy minimization).

In Appendix B, we derive a lemma which shows how the time integral of an operator in the Heisenberg representation can be expanded into a series of operators, in the interaction representation, involving commutators with the interaction Hamiltonian  $W_I$ . Hence the integral  $\int_{-\infty}^0 J_S(u) du$  entering the definition of  $\rho^{\text{NESO}}$  can be expanded in a series similar to that obtained for the  $Y^{E,Q}$  operators defining of the generalised NE density matrix.

We now proceed with the formal derivation of the connection between Eq. (17) and Eq. (24). For that we first note that

$$\begin{aligned} J_S(s) &= i \sum_{\alpha} [H, \beta_{\alpha} H_{\alpha}(s) - \beta_{\alpha} \mu_{\alpha} N_{\alpha}(s)] \\ &= i \sum_{\alpha} e^{iHs} [W, \beta_{\alpha} H_{\alpha} - \beta_{\alpha} \mu_{\alpha} N_{\alpha}] e^{-iHs}, \end{aligned} \quad (26)$$

then we rewrite  $\sum_{\alpha} \beta_{\alpha} H_{\alpha}$  as follows

$$\begin{aligned} \beta_L H_L + \beta_R H_R &= \bar{\beta} (H_L + H_R + W) \\ &\quad - \bar{\beta} W + (\beta_L - \bar{\beta}) H_L + (\beta_R - \bar{\beta}) H_R \\ &= \bar{\beta} (H - W + Y_0^E) \end{aligned} \quad (27)$$

with the help of Eq. (19).

Hence the NE statistical operator in Eq. (24) can be reformulated as

$$\begin{aligned} \rho^{\text{NESO}} &= \frac{1}{Z} \exp - \bar{\beta} \left\{ H - W + Y_0^E - Y_0^Q \right. \\ &\quad \left. - \int_{-\infty}^0 ds e^{\eta s} J_S(s) / \bar{\beta} \right\}. \end{aligned} \quad (28)$$

The integral of the non-systematic energy flows is obtained from different contributions:

$$\int_{-\infty}^0 ds e^{\eta s} J_S(s) / \bar{\beta} = B^Q + B_{\text{tot}}^E, \quad (29)$$

where

$$\begin{aligned} B^Q &= \int_{-\infty}^0 ds e^{\eta s} e^{iHs} (-i) [W, \sum_{\alpha} \beta_{\alpha} \mu_{\alpha} N_{\alpha} / \bar{\beta}] e^{-iHs} \\ &= \int_{-\infty}^0 ds e^{\eta s} e^{iHs} (-i) [W, Y_0^Q] e^{-iHs}. \end{aligned} \quad (30)$$

and

$$\begin{aligned} B_{\text{tot}}^E &= \int_{-\infty}^0 ds e^{\eta s} e^{iHs} i [W, \sum_{\alpha} \beta_{\alpha} H_{\alpha} / \bar{\beta}] e^{-iHs} \\ &= \int_{-\infty}^0 ds e^{\eta s} e^{iHs} (i [W, H - W + Y_0^E]) e^{-iHs}, \end{aligned} \quad (31)$$

using Eq. (27). The commutator in Eq. (31) contains three terms, the first is simply the time derivative of the operator  $W$  in the Heisenberg representation:  $\partial_s W_H(s) = e^{iHs} i [H, W] e^{-iHs}$ . Hence the time integral (with the adiabatic factor) simply gives the value  $-W_H(s=0) = W$ . The second term in the commutator vanishes, while the third term is:

$$-B^E = \int_{-\infty}^0 ds e^{\eta s} e^{iHs} (i [W, Y_0^E]) e^{-iHs}. \quad (32)$$

Hence

$$\int_{-\infty}^0 ds e^{\eta s} J_S(s) / \bar{\beta} = B^Q - W - B^E, \quad (33)$$

and the NE statistical operator  $\rho^{\text{NESO}}$  can be rewritten in a compact form similar to Eq. (17):

$$\rho^{\text{NESO}} = \frac{1}{Z} e^{-\bar{\beta} (H - \Upsilon^Q + \Upsilon^E)}, \quad (34)$$

with  $\Upsilon^x = Y_0^x + B^x$  and  $x \equiv Q, E$ . We can now prove that the quantities  $\Upsilon^{Q,E}$  obey the same series iterative expansion as their counterparts  $Y^{Q,E}$  in Eq. (18). This is readily done by using the Peletminskii lemma described in Appendix B. Indeed according to the lemma, the quantity  $B^x = \int_{-\infty}^0 ds e^{\eta s} e^{iHs} (-i [W, Y_0^x]) e^{-iHs}$  is strictly equal to

$$\begin{aligned} B^x &= \int_{-\infty}^0 ds e^{\eta s} e^{iH_0 s} (-i [W, Y_0^x] - i [W, B^x]) e^{-iH_0 s} \\ &= -i \int_{-\infty}^0 ds [\tilde{W}_I(s), Y_0^x] - i \int_{-\infty}^0 ds [\tilde{W}_I(s), B_I^x(s)]. \end{aligned} \quad (35)$$

The first commutator in the left-hand-side of Eq. (35) is just the definition of the time derivative of the quantity  $Y_{1,I}^x(s)$ , as  $\partial_s Y_{1,I}^x(s) = -i [\tilde{W}_I(s), Y_0^x]$ . Hence the corresponding integral simply gives  $Y_{1,I}^x(s=0) - Y_{1,I}^x(s=-\infty) = Y_{1,I}^x(s=0)$ , as we assume that  $\tilde{W}_I(s)$  vanishes at  $s = -\infty$ . Therefore we have,

$$B^x = Y_{1,I}^x(s=0) - i \int_{-\infty}^0 ds [\tilde{W}_I(s), B_I^x(s)], \quad (36)$$

By inserting the definition of  $B^x$  itself in the right-hand-side commutator of Eq. (36), we obtain the series expansion

sion

$$B^x = Y_{1,I}^x(0) + \int_{-\infty}^0 ds [-i\tilde{W}_I(s), Y_{1,I}^x(s)] \\ + \int_{-\infty}^0 ds [-i\tilde{W}_I(s), \int_{-\infty}^s ds_1 [-iW_I(s_1), \int_{-\infty}^{s_1} ds_2 \\ [-i\tilde{W}_I(s_2), Y_0^x]]] + \dots \quad (37)$$

Hence we obtain the expected series expansion  $\Upsilon^x = Y_0^x + Y_{1,I}^x + Y_{2,I}^x + \dots$  where the different terms of the series are given by the iterative scheme  $Y_{n+1,I}^x = \int_{-\infty}^0 ds [-i\tilde{W}_I(s), Y_{n,I}^x(s)]$ , or equivalently by the differential equations defined in Eq. (18).

We have therefore proven in an accurate formal way that there is a one-to-one correspondence between our generalisation of the NE density matrix postulated in Sec. IV and the exact general form of the McLennan-Zubarev NE statistical operation Eq. (24), henceforth proving (*a posteriori*) the validity of our results given in Sec. IV.

## VI. AN EXAMPLE

We now show an example for the lowest order expansion of the NE density matrix by considering a non-interacting system and a simple description for the central region  $C$ .

In the absence of interaction, the Hamiltonian for the central region  $C$  is simply given by  $H_C^0 = \varepsilon_0 d^\dagger d$  where  $d^\dagger$  ( $d$ ) creates (annihilates) an electron in the level  $\varepsilon_0$ . The non-interacting electrodes are also described by a quadratic Hamiltonian  $\alpha = L, R$  with  $H_\alpha = \sum_{k\alpha} \varepsilon_{k\alpha} c_{k\alpha}^\dagger c_{k\alpha}$  where  $k\alpha$  is an appropriate composite index to label the free electrons of the  $\alpha$  electrode. The coupling between the central region and the electrodes is given via some hopping matrix elements  $t_{k\alpha}$ , and we have  $\sum_\alpha (V_{C\alpha} + V_{\alpha C}) = \sum_{k,\alpha} t_{k\alpha} (c_{k\alpha}^\dagger d + d^\dagger c_{k\alpha})$ . We recall that, by definition, we have  $W = H_C^0 + \sum_\alpha (V_{C\alpha} + V_{\alpha C})$ , and that the only non vanishing anti-commutators are  $\{d, d^\dagger\} = 1$  and  $\{c_{k\alpha}, c_{p\beta}^\dagger\} = \delta_k \delta_{\alpha\beta}$ .

We now proceed to calculate the operators  $Y^x$  ( $x = Q, E$ ) from the iterative scheme developed in Sec. IV. The zero-Th order is given by the definition of the operators  $Y_0^x$ , i.e.  $Y_0^Q = a_L^Q N_L + a_R^Q N_R$  and  $Y_0^Q = a_L^E H_L + a_R^E H_R$  from Eq.(19). Note that we introduced (for later convenience) a new notation for  $Y_0^Q$  where  $a_L^E = a^E = -a_R^E$  from Eq.(19).

The first order contribution  $Y_{1,I}^x$  involves the calculation of the commutator  $[W, Y_0^x]$  which is built from three different kinds of commutators  $[d^\dagger d, c_{k\alpha}^\dagger c_{k\alpha}]$ ,

$[c_{p\beta}^\dagger d, c_{k\alpha}^\dagger c_{k\alpha}]$ ,  $[d^\dagger c_{p\beta}, c_{k\alpha}^\dagger c_{k\alpha}]$ . We find

$$[W, Y_0^Q] = \sum_\alpha a_\alpha^Q \sum_k t_{k\alpha} (d^\dagger c_{k\alpha} - c_{k\alpha}^\dagger d) \\ = i \sum_\alpha a_\alpha^Q j_\alpha^Q, \quad (38)$$

with the conventional definition of the charge current operator  $j_\alpha^Q = -i \sum_k t_{k\alpha} (d^\dagger c_{k\alpha} - c_{k\alpha}^\dagger d)$ ; and

$$[W, Y_0^E] = i \sum_\alpha a_\alpha^E j_\alpha^E, \quad (39)$$

with the definition of the energy current operator  $j_\alpha^E = -i \sum_k \varepsilon_{k\alpha} t_{k\alpha} (d^\dagger c_{k\alpha} - c_{k\alpha}^\dagger d)$  by analogy with the definition of the charge current. Therefore, the first order contribution  $Y_{1,I}^x$  is obtained from

$$Y_{1,I}^x = \sum_\alpha a_\alpha^x \int_{-\infty}^0 ds e^{\eta s} j_{\alpha,I}^x(s), \quad (40)$$

with  $j_{\alpha,I}^x(s)$  being the interaction representation of  $j_\alpha^x$  ( $x = Q, E$ ). Such a result can also be obtained, in a more straightforward way, from the expression of the NESO given in Eq. (24). Indeed, the first order contribution  $Y_{1,I}^x$  is simply obtained from the integral of the non-systematic energy flow by replacing the Heisenberg representation of  $J_S(s)$  by its lowest order expansion in the interaction representation.

Interestingly, one can introduce an advanced quantity  $f^{\text{adv}}(s)$  by defining  $f^{\text{adv}}(s) = \theta(-s) e^{\eta s} f(s)$ . Hence the time integral in Eq. (40) becomes the Fourier transform  $\int_{-\infty}^{\infty} ds j_{\alpha,I}^{x,\text{adv}}(s)$  of  $j_{\alpha,I}^{x,\text{adv}}(s)$  evaluated at  $\omega = 0$ . The first order contributions

$$Y_{1,I}^x = \sum_\alpha a_\alpha^x j_{\alpha,I}^{x,\text{adv}}(\omega = 0) \quad (41)$$

are then related to the static (d.c.) limit of the current operators.

The higher order contributions are more cumbersome to evaluate explicitly. For example, the second order contributions are given by

$$Y_{2,I}^x = \int_{-\infty}^0 ds e^{\eta s} [-i\tilde{W}_I(s), Y_{1,I}^x(s)] = \sum_\alpha a_\alpha^x \\ \int ds \int ds_1 e^{\eta s} e^{\eta s_1} e^{iH_0 s} [-iW, j_{\alpha,I}^x(s_1 - s)] e^{-iH_0 s}. \quad (42)$$

Their evaluation involves not only the calculation of the commutator between  $W$  and  $j_\alpha^x$  but also the series expansion of  $j_{\alpha,I}^x$  in terms of  $H_0$ .

For any perturbation series expansion, the results given by a lowest order expansion of the NE density matrix will always be different from the exact (fully resummed) results. We provide, in Appendix C, a brief analysis of

the errors introduced by a finite series expansion of the  $Y^{Q,E}$  operators.

One can also draw some analogies between our results and the results for the expression of the operator  $Y$  (system at a unique  $T$ ) given in Ref. [22]. This can be done by introducing the definition of the advanced Green's function  $g_0^{\text{adv}}(\omega) = i \int ds e^{\eta s} \theta(-s) e^{\pm i H_0 s} e^{i \omega s} = [\omega \pm H_0 - i\eta]^{-1}$ . Furthermore the central quantities, in the interaction representation of the current operators, are  $e^{i H_0 s} d^\dagger c_{k\alpha} e^{-i H_0 s}$  and  $e^{i H_0 s} c_{k\alpha}^\dagger d e^{-i H_0 s}$ . This quantities can be re-expressed as follows

$$\begin{aligned} e^{i H_0 s} d^\dagger c_{k\alpha} e^{-i H_0 s} &= -d^\dagger c_{k\alpha} (1 + e^{-i \varepsilon_{k\alpha} s} e^{-i H_0 s}) \\ e^{i H_0 s} c_{k\alpha}^\dagger d e^{-i H_0 s} &= -c_{k\alpha}^\dagger d (1 - e^{i \varepsilon_{k\alpha} s} e^{-i H_0 s}), \end{aligned} \quad (43)$$

and the time integration of the corresponding time-dependent factors will lead to the appearance of the Green's functions in the series expansion of the  $Y^{Q,E}$  terms.

One should however note that, by definition, our results are formally different from the expression of the operator  $Y$  given in Ref. [22]. We are dealing with a general problem where  $\beta_L \neq \beta_R$  and  $\mu_L \neq \mu_R$  and the possibility of an asymmetric potential drop, i.e. our  $\mu_\alpha$  are different from the symmetric case  $\mu_L = V/2 = -\mu_R$ . Furthermore, our expressions will be different from the results of Ref. [22] since we are using a different initial density matrix  $\rho_0 = \rho_L \otimes \rho_R$ . We do not consider that initial the central region is described by a canonical ensemble  $\rho_C \neq e^{-\beta H_C^0}/Z$  as explained in detail in Sec. II B.

Finally, we briefly comment on possible extensions to systems where the interaction is not only limited to the central region. We suggest that the essential point is that the reservoirs are indeed described by an equilibrium density matrix, hence interaction may exist in them and throughout the entire system. However, when considering the iterative scheme to calculate the  $Y^{E,Q}$  quantities, one can anticipate that each iteration will involve operators which get more and more spread all over the entire system (when interaction exist inside the leads). This point might then lead to strong computational constraints in comparison to the cases where the interaction is present only in the central region.

## VII. CONCLUSION

We have proposed how to expand the NE density matrix originally developed by Hershfield to the cases of simultaneous (steady state) current flows of heat and charge. The stationary density matrix of an open system is written in the generalised Gibbs form  $\rho^{\text{NE}} = e^{-\beta(H - Y^Q + Y^E)}/Z$ , with the nonequilibrium ‘‘correction terms’’  $Y^{Q,E}$  being related to the charge and energy currents imposed by the NE conditions. We have provided an explicit iterative scheme to calculate the  $Y^{Q,E}$  operators which is similar to the iterative scheme developed originally by Hershfield.

We have also proved in a rigorous way that our generalised NE density matrix is strictly equivalent to the McLennan-Zubarev form of the NE statistical operator, validating *a posteriori* the correctness of our scheme.

The operator  $\bar{\beta}(Y^E - Y^Q)$  is related to the entropy production of the NE quantum open system<sup>53</sup>. It can be calculated in the absence and in the presence of interaction and gives information about the dissipation in the driven system. We have provided an explicit example for the lowest order expansion of the NE density matrix for a non-interacting model system.

The generalized scheme to calculate the NE density matrix that we have presented here can now serve as the basis for numerical calculations of both heat and charge transport using the numerical techniques developed on the original approach of Hershfield<sup>22–28</sup>. As clearly shown in Ref.[31], the NE density matrix has variational properties and hence can also be used to define a rigorous single-particle scheme in the spirit of a density-functional-based theory (once the proper NE functionals are properly set up)<sup>31</sup>.

The NE density matrix can also lead to more insight for the NE physical properties of quantum open systems and to the derivation of NE thermodynamical laws, such as NE fluctuation-dissipation relations<sup>58</sup>, NE electron distribution function<sup>59</sup> and NE charge susceptibility<sup>60</sup>.

Finally, we would like to make two general comments. First, we briefly comment on the connections between the NE density matrix and the more widely use NE Green's functions (GF) approaches. The GF are correlation functions whose thermodynamical averages are formally identical to those calculated in Hershfield approach (which we generalized in the present paper for the cases of two reservoirs at different chemical potentials and temperatures). As we explained in Ref. [52], both perturbation series used in the NE GF approach and in the derivations of the equations for the  $Y^{Q,E}$  operators start from the same nonequilibrium series expansion. They are two different ways of summing that series. For a non-interacting problem for which the series can be resumed exactly, the NE GF and the Hershfield  $Y$  operator approach provide the same results<sup>20,21</sup>. For an interacting system, one must resort to approximations to re-sum partially the series, and therefore the two approaches are similar only when the same level of approximations are used<sup>22,61,62</sup>.

Second, we want to point out that various authors have constructed a number of theoretical schemes for the description of irreversible processes in NE systems. In this paper, we have focussed on the approaches developed by Hershfield and Zubarev. Other schemes have been developed by Peletninskii *et al.* to find expressions for the NE density matrix<sup>57,63–65</sup>. A critical study of the equivalence between the two kinds of methods can be found in Ref. [66]. It is interesting to note that in the Peletninskii approaches, the solution is related to a series expansion of the density matrix, as obtained from a perturbation expansion of the solution of the Liouville equation for the density matrix (and with the appropri-



ate sources term that ensure the irreversible nature of the time evolution)<sup>67</sup> In the other approaches, the NE density matrix is also given by a series expansion but rather in the form of a linked-cluster-like expansion<sup>68</sup>, i.e. the corresponding series expansion enters the argument of an exponential functional. In principle, if all the resummations are performed exactly the two kinds of approach are also equivalent.

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### Appendix A: The Møller operators for scattering

By definition<sup>46–49</sup>, the Møller operators are given for two asymptotic limits:

$$\Omega^{(\pm)} = \lim_{t \rightarrow \mp\infty} e^{iHt} e^{-iH_0 t}. \quad (\text{A1})$$

corresponding to retarded or advanced evolution of the system. Alternatively, the Møller operators can be also expressed in an integral form<sup>47–49</sup>:

$$\Omega^{(\pm)} = \lim_{\eta \rightarrow 0^+} (\mp\eta) \int_0^{\mp\infty} du e^{\pm\eta u} e^{iHu} e^{-iH_0 u}. \quad (\text{A2})$$

They follow the intertwining property:  $\Omega^{(\pm)} H_0 = H \Omega^{(\pm)}$  which we now prove for  $\Omega^{(+)}$ . We start by writing:

$$\begin{aligned} \Omega^{(+)} &= \lim_{\eta \rightarrow 0^+} \int_{-\infty}^0 d\tau \eta e^{\eta\tau} e^{iH\tau} e^{-iH_0\tau} \\ &= \lim_{\eta \rightarrow 0^+} \int_{-\infty}^0 d\tau \eta e^{\eta\tau} \bar{S}(\tau). \end{aligned} \quad (\text{A3})$$

It can be seen that  $\bar{S}(\tau)$  obeys the following differential equation:  $\partial_\tau \bar{S}(\tau) = i\bar{S}(\tau)W_I(\tau)$ . Hence

$$\begin{aligned} H\Omega^{(+)} &= \lim_{\eta \rightarrow 0^+} \int_{-\infty}^0 d\tau \eta e^{\eta\tau} e^{iH\tau} H e^{-iH_0\tau} \\ &= \Omega^{(+)} H_0 + \lim_{\eta \rightarrow 0^+} \int_{-\infty}^0 d\tau \eta \bar{S}(\tau) \tilde{W}_I(\tau), \end{aligned} \quad (\text{A4})$$

where the adiabatic term has been included in  $\tilde{W}_I(\tau)$ . The integral in Eq. (A4) becomes

$$\begin{aligned} \eta \int_{-\infty}^0 d\tau \bar{S}(\tau) W_I(\tau) &= -i\eta \int_{-\infty}^0 d\tau \partial_\tau \bar{S}(\tau) \\ &= -i\eta [\bar{S}(\tau)]_{-\infty}^0 = -i\eta (1 - \bar{S}(-\infty)), \end{aligned} \quad (\text{A5})$$

and vanishes in the limit  $\eta \rightarrow 0^+$  since  $\bar{S}(-\infty) = \bar{S}(-\infty)^\dagger = \Omega^{(+)-1}$  is finite.

Hence the relation  $H\Omega^{(+)} = \Omega^{(+)} H_0$  is proved.

### Appendix B: The Peletminskii Lemma

In this section, we consider a useful Lemma given by Peletminskii in the Appendix of Ref. [57]. We rederive the lemma below since we use a different sign convention and include an adiabatic factor  $e^{\eta x}$ .

The lemma provides, in an integral form, a connection between the Heisenberg representation of an operator and the corresponding series expansion of operators in the interaction representation.

Suppose that, for an arbitrary operator  $A$ , we define

$$B = \int_{-\infty}^0 dx e^{\eta x} e^{iHx} A e^{-iHx} = \int_{-\infty}^0 dx e^{\eta x} A_H(x) \quad (\text{B1})$$

where  $A_H(x)$  is the Heisenberg representation of  $A$  with respect to the total Hamiltonian  $H = H_0 + W$ , and  $\eta \rightarrow 0^+$ .

Introducing, an intermediate quantity:

$$\bar{A}(x) = e^{-iH_0 x} e^{iHx} A e^{-iHx} e^{iH_0 x}, \quad (\text{B2})$$

we can see that  $\bar{A}(x)$  follows the differential equation  $\partial_x \bar{A}(x) = i[W_I(-x), \bar{A}(x)]$  since the quantity  $P(x) = e^{-iH_0 x} e^{iHx} = \bar{S}^{-1}(-x)$  obeys  $\partial_x P(x) = iW_I(-x)P(x)$ . Hence

$$\bar{A}(\tau) = A + i \int_0^\tau dx [W_I(-x), \bar{A}(x)], \quad (\text{B3})$$

where  $W_I(x)$  is the interaction representation of  $W$ :  $W_I(x) = e^{iH_0 x} W e^{-iH_0 x}$ .

By reversing the definition Eq. (B2) and using Eq. (B3), we find that

$$\begin{aligned} B &= \int_{-\infty}^0 dx e^{\eta x} e^{iH_0 x} A e^{-iH_0 x} \\ &\quad + i \int_{-\infty}^0 dx e^{\eta x} \int_0^x dy e^{iH_0 y} [W_I(-y), \bar{A}(y)] e^{-iH_0 y}. \end{aligned} \quad (\text{B4})$$

Now, we follow two steps of calculation: (1) use the definition of  $W_I(-y)$  and change the variable  $y$  into  $v = x - y$ , and (2) use the definition of  $\bar{A}(x)$ , to transform Eq. (B4) into

$$\begin{aligned} B &= \int_{-\infty}^0 dx e^{\eta x} e^{iH_0 x} A e^{-iH_0 x} \\ &\quad - i \int_{-\infty}^0 dx e^{\eta x} \int_x^0 dv e^{iH_0 v} [W, A_H(x-v)] e^{-iH_0 v}. \end{aligned} \quad (\text{B5})$$

Finally, by swapping the order of the integrals  $\int_{-T}^0 dx \int_x^0 dv \rightarrow \int_{-T}^0 dv \int_{-T}^v dx$  (with  $T \equiv \infty$ ), and identifying  $\int_{-\infty}^v dx e^{\eta x} e^{iH(x-v)} A e^{-iH(x-v)} = e^{\eta v} B$ , we ob-

tain the following lemma:

$$\begin{aligned} B &= \int_{-\infty}^0 dx e^{\eta x} e^{iHx} A e^{-iHx} \\ &= \int_{-\infty}^0 dx e^{\eta x} e^{iH_0 x} (A - i[W, B]) e^{-iH_0 x}. \end{aligned} \quad (\text{B6})$$

Eq. (B6) connects, in an integral form, the Heisenberg representation of  $A$  with a series expansion of commutators ( $\dots [W, [W, A] \dots]$ ) in the interaction representation. The lemma Eq. (B6) is central to our proof of the equivalence between the NE density matrix  $\rho^{\text{NE}}$  and the McLennan-Zubarev NE statistical operator.

### Appendix C: Convergence of the expected values

One can perform the calculation of the NE density matrix by using only a finite number of terms in the series expansion of the  $Y^{Q,E}$  (in Sec. VI we show only the two first terms). We call the corresponding NE density matrix  $\rho_{(n)}^{\text{NE}}$ , it is obtained from the lowest  $n$ -terms in the series expansion of the operators

$$Y_{(n)}^{Q,E} = \sum_{i=0}^n Y_{i,I}^{Q,E}, \quad (\text{C1})$$

instead of the full series given by Eq. (18)

The corresponding error induced the average of any operator  $X$  is given by:

$$\begin{aligned} \delta \langle X \rangle_{(n)}^{\text{NE}} &= \text{Tr}[\rho^{\text{NE}} X] - \text{Tr}[\rho_{(n)}^{\text{NE}} X] \\ &= \text{Tr}[(\rho^{\text{NE}} - \rho_{(n)}^{\text{NE}}) X], \end{aligned} \quad (\text{C2})$$

with  $\rho_{(n)}^{\text{NE}} = \exp(-\bar{\beta}(H - Y_{(n)}^Q + Y_{(n)}^E))/Z_{(n)}$  and the partition function  $Z_{(n)} = \text{Tr}[\rho_{(n)}^{\text{NE}}]$ .

We can now proceed with an analysis in terms of the power of the interaction  $W^n$ . Both partition functions  $Z = \text{Tr}[\rho^{\text{NE}}]$  and  $Z_{(n)}$  contain all orders of the interaction  $\mathcal{O}(W^n)$  with  $n = 0, 1, 2, 3, \dots$ . In order to get the leading term (lowest power of  $W^n$ ) in  $\delta \langle X \rangle_{(n)}^{\text{NE}}$ , we can just consider the difference of the two exponentials in the NE densities. At the lowest order, it is easily found that

$$\begin{aligned} e^{-\bar{\beta}(H - Y^Q + Y^E)} - e^{-\bar{\beta}(H - Y_{(n)}^Q + Y_{(n)}^E)} \\ \sim \sum_{i=n+1}^{\infty} \bar{\beta}(Y_{i,I}^Q - Y_{i,I}^E), \end{aligned} \quad (\text{C3})$$

which gives a leading term in  $\mathcal{O}(W^{n+1})$ .

Therefore, for the calculations shows in Sec. VI, if we consider only the terms up to  $n = 1$ , the error is (for the non-interacting case) in  $t_{k\alpha}^2$ . Such a lowest order expansion is only expected to be valid in the limit of weak coupling between the central region and the electrodes.

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- <sup>51</sup> By construction, the NE density matrix commutes with the total Hamiltonian  $H$ . Such a commutation property could lead wrong results about the description of the NE total internal energy in terms of the initial eigenstates. A complete discussion related to this issue is given in Section 5 of Ref. [31].
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